

Resolving natural and anthropogenic sources of solutes to a watershed from historic mining

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ABSTRACT: In catchments with mineral deposits, it is often difficult or impossible to distinguish between the contributions of solutes derived from historic mining activities versus natural inputs. This problem is compounded by the fact that mineralized areas can have high natural background concentrations of some metals and anions, as well as low pH. In this study, spatially dense sampling of surface waters and springs provided sufficient information to estimate the relative contributions of some metals to a stream from natural and anthropogenic sources. Numerical modeling of the field results showed that Al and Fe oxyhydroxides exceed saturation in places where they are observed to be precipitating. Concentrations of trace metals such as Cu, Pb, and Zn in model mixtures, compared to actual samples, show the role of adsorption in retarding the transport of trace metals, but also shows that in many reaches of the stream, the trace metals behave conservatively. The approach described here represents a useful strategy for examining the effects of historic mining in alpine catchments.

1 INTRODUCTION

In the western USA, there are thousands of historic mines, most of which are abandoned. Many of these mines were active more than 50 to 100 years ago, and now it is impossible to know the true pre-mining chemistry of either surface or ground water. In some cases, it has been possible to show that pre-mining water chemistry already showed substantial effects from natural weathering of local mineral deposits (cf. Furniss & Hinman 1998) or to make more precise estimates of pre-mining chemical conditions (Miller & McHugh 1999) based on sampling and numerical modeling. Recent studies have examined metal concentrations in individual tree rings to determine availability of metals to the environment (Witte et al., in press), providing an indication of the existence of metals in soils, but not in waters.

In this study, extensive, spatially dense sampling was conducted in an alpine catchment in central Colorado, USA, which has been affected by high natural background concentrations of some metals and acidic, metal-rich drainage from an abandoned mine. The Redwell basin (Fig. 1) is a small high-gradient catchment, and contains sub-surface (>750 m below land surface) porphyry-style molybdenum mineralization (E in Fig. 1) and near-surface polymetallic vein mineralization. Sulfide minerals in the latter consist primarily of pyrite, galena, and sphalerite. The porphyry systems have been deline-

ated by drilling (Thomas & Galey 1982) and the vein systems have been mined historically. The Redwell basin also is host to a natural, ferricrete-depositing spring (the “Red Well,” D in Fig. 1); ^{14}C dating of organic material entrained in the ferricrete is as old as 2800 ^{14}C years before present (Fall 1997).

1.1 Sampling

In 1997, 2000, 2001 and 2002, we conducted a series of sampling trips. In 2001 we collected more than 75 samples along the 2 km of Redwell Creek as we conducted an in-stream tracer test (e.g. Kimball et al. 2002). The spatially dense sample set provides the opportunity to characterize all the inputs of ground water and surface water to Redwell Creek, and is the basis for this paper.

Samples were collected according to established methods (USGS 2004); all water samples were filtered through 0.45 μm filters and acidified to pH \sim 1 with ultrapure HNO_3 . Cations were measured on the filtered, acidified samples by ICP-MS and ICP-AES (Briggs 2002, Lamothe et al. 2002). Filtered, unacidified samples were kept cold ($<4^\circ\text{C}$) and brought back to the lab for anion analysis by ion chromatography (Theodorakos et al. 2002). Temperature, conductivity, pH, dissolved oxygen, and Fe^{2+} were measured at each site at the time of sample collection.

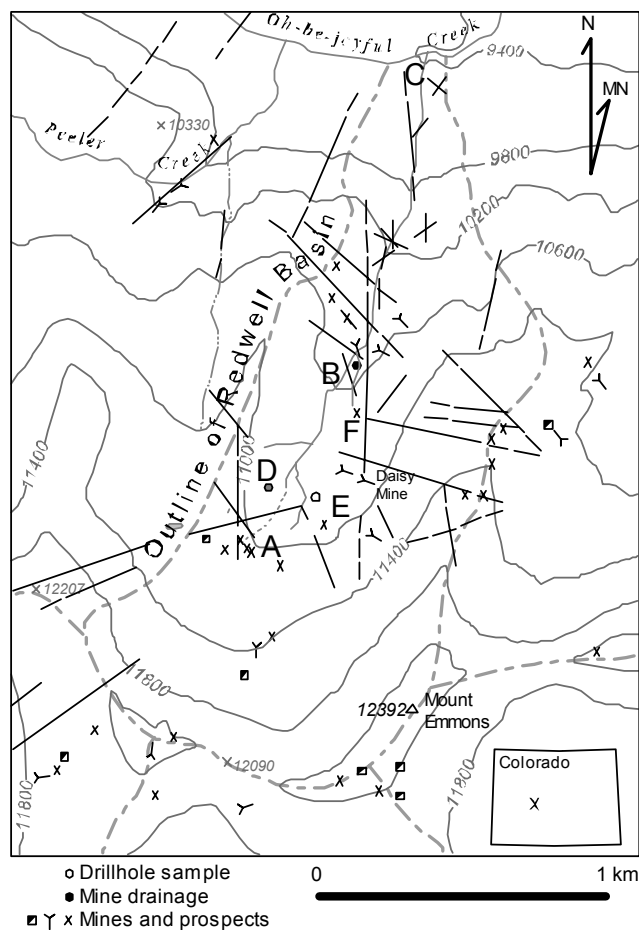


Figure 1. The Redwell basin in western Colorado. Solid straight lines indicate fractures and faults, dashed where uncertain or obscured. Dashed gray lines indicate drainage boundaries. Letters A-F are explained in the text. Contours are in feet above mean sea level, contour interval 400 feet (approx. 125 meters).

2 RESULTS

2.1 Major tributaries to Redwell Creek

In the most upstream reach (A in Fig. 1), Redwell Creek shows little effect of the pervasive mineralization in the catchment. The pH is 6.5, and the ionic strength is ca. 1×10^{-3} m. Addition of water from a prospect (shown by the "x" below left of the letter E in Fig. 1) causes the pH to drop slightly, and the streambed is coated with a white precipitate, presumably Al-oxyhydroxides. With further additions of acidic water (pH < 4) from an artesian exploration well and the natural "Red Well" (just left of "E," and "D," respectively, in Fig. 1), the streambed abruptly changes to a red-ochre color and is completely cemented by Fe-oxyhydroxides for more than 100 m. With the addition of drainage from the Daisy Mine (F in Fig. 1), pH remains low and metals concentrations incrementally increase (Fig. 2). Downstream from the input of water from the Daisy Mine, the pH of Redwell Creek is 3.75 and the ionic strength is about 4×10^{-3} m.

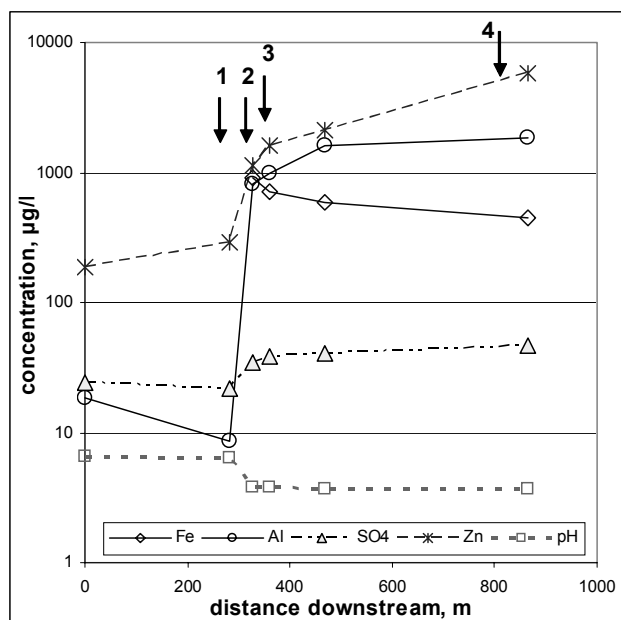


Figure 2. Concentrations of Fe, Al, SO₄, Zn, and pH in Redwell Creek. Numbered arrows denote locations of major tributaries: 1- the prospect adit; 2- the artesian well; 3- the Red Well; and 4- the Daisy mine.

Mixing relationships of tributaries shown in Figure 1 form the basis for numerical modeling using PHREEQC (Parkhurst & Appelo 1999). During our field sampling, we collected triplets of samples at each tributary point - a sample of the tributary as well as samples of Redwell Creek upstream and downstream of the tributary. In the PHREEQC modeling, the upstream sample of Redwell Cr. was numerically mixed with the tributary in a proportion determined using a ternary diagram and the lever rule (cf. Ehlers 1972; Fig. 3). In some cases, the mixing proportions were adjusted slightly so that the major cations (Ca, Mg, Na, & K) behaved conservatively; that is, their concentration in the model mixture equaled that in the downstream sample. The model mixture was compared with the downstream sample collected below the mixing zone to determine which of the other elements appear to mix conservatively and which do not. Of the four mixing zones, three of the tributaries are anthropogenic and one, the Red Well, represents a natural input. These will be discussed in order of their entrance into Redwell Creek.

2.1.1 Mixing with drainage from the prospect adit

Upon mixing with the acidic (pH 4.3) drainage from the prospect adit, the pH in Redwell Creek drops to 6.4 and Al-oxyhydroxides precipitate. In the model results, amorphous Al-oxyhydroxide is undersaturated (SI = -1.2), but gibbsite is supersaturated (SI = +1.6), so it is presumed that an intermediate phase, or one with different components, is forming in the mixing zone (cf. Nordstrom 1982; May 1992). Comparing the actual sample from the mixing zone

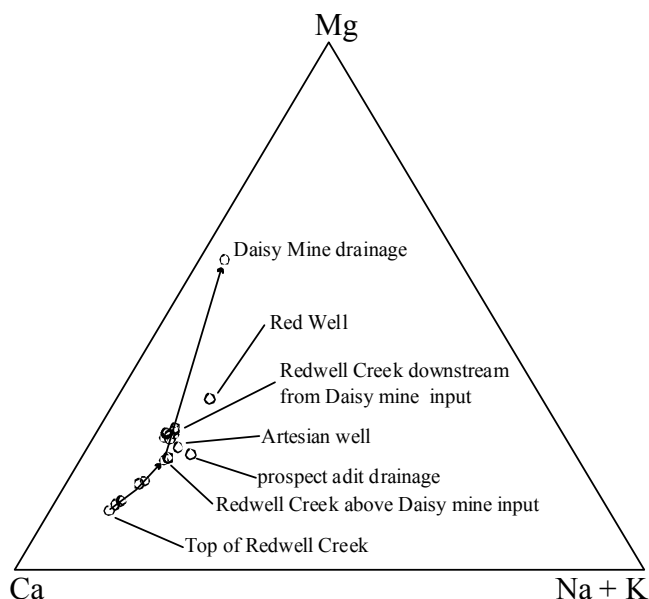


Figure 3. Trilinear diagram showing the evolution of water chemistry along Redwell Creek. The lever rule can be used to determine mixing proportions.

with the model mixture reveals that the actual Al concentration is about 7% of what would be expected for conservative mixing. In other words, about 93% of the Al has precipitated as a result of the mixing. Iron was below detection in these samples, but Mn was present. Manganite, MnOOH , was supersaturated and it appears that 50-60% of the Mn precipitated in the mixing zone compared to what would be expected if mixing were conservative. Cu, Pb, and Zn show varying degrees of removal, presumably by adsorption to fresh precipitates, with 75%, 80%, and 15% depletion, respectively, in the mixture. SO_4^{2-} behaves conservatively.

2.1.2 Mixing with the artesian exploration well

In the mixing zone with the artesian well, pH drops significantly to 3.77, and Fe-oxyhydroxides abruptly precipitate. In the numerical simulations, Al-oxyhydroxides are undersaturated ($\text{Al}(\text{OH})_{3(\text{am})}$ SI = -5.3; gibbsite SI = -2.5), but $\text{Fe}(\text{OH})_3$ is at saturation. Comparing the numerical mixture to the actual sample reveals that Al and Mn behave conservatively, but about 33% of the Fe has precipitated. In this low-pH environment, Cu shows < 10% adsorption; SO_4^{2-} , Pb and Zn behave conservatively.

2.1.3 Mixing with the Red Well

Upon mixing with the Red Well, the pH of Redwell Cr. remains the same (pH 3.80), and Fe-oxyhydroxides continue to precipitate. About two-thirds of the Fe precipitates in this mixing zone compared to ideal conservative mixing (SI of $\text{Fe}(\text{OH})_{3(\text{am})}$ in the ideal mixture is +0.12), but Al and Mn behave conservatively. In the low-pH environment, little adsorption of trace metals is expected,

and little is observed, as the ratios of SO_4^{2-} , Cu, Pb, and Zn in the mixture compared to the actual samples is within a few percent of unity in all cases.

2.1.4 Mixing with the Daisy Mine drainage

Mixing with the Daisy Mine drainage is hydrologically more complicated because a talus slope distributes the water away from a single, well-defined channel and there are numerous diffuse inputs along this reach of 10-20 m where the toe of the talus slope is in Redwell Creek. For that reason, the mixing zone is more diffuse than in the previous cases, and our sample might not be representative of the complete input from the Daisy Mine. Nevertheless, it is still possible to carry out an analysis similar to those of the upstream inputs. The pH of the Daisy Mine drainage is 3.09, and mixing of this drainage with Redwell Cr. causes the latter to drop to pH 3.66. Fe continues to precipitate - more than 85% depletion in Fe is observed between the model mixture and the actual sample from below the mixing zone; the SI of $\text{Fe}(\text{OH})_{3(\text{am})}$ is 0. From the PHREEQC models, it appears that Cu and Zn may adsorb (or co-precipitate) slightly, as both show about 30% depletion in the actual sample relative to the ideal mixture, but this result might be spurious, and related to the hydrologic complexities discussed above. Another line of evidence suggesting that our sample is not entirely representative is in the Mn result; Mn appears to be twice as great as would be expected from conservative mixing, indicating another source of Mn. SO_4^{2-} decreases by about 25 %.

3 METAL LOADS FROM VARIOUS SOURCES

Metal loads were calculated for each of the four sources described above, using streamflow as determined by the tracer dilution method (e.g. Kimball et al. 2002). Using this method, streamflow was calculated based on the observed dilution of a Li tracer injected at the most upstream site. Accuracy of flow determined in this way is similar to the analytical accuracy of the tracer, <10 % relative error.

With the incremental addition of drainage from the four sources described above, only Zn and SO_4^{2-} increase at each step. Cu, Pb, Mn, Fe, and Al all decrease in at least one of the tributary points - this result is likely due to precipitation of Fe, Mn, or Al oxyhydroxides and adsorption or coprecipitation of Cu and Pb. As noted in the above discussion, Zn and SO_4^{2-} do not always behave conservatively, but nearly so in most cases. The remaining discussion will focus on the results for these two constituents.

The total (dissolved + suspended) loads of Zn and SO_4^{2-} downstream of the Daisy Mine input are 0.13 and 3.6 g/s. The four inputs described above account for > 75% of the total Zn load and ~50% of the SO_4^{2-}

load in Redwell Creek. Table 1 shows the relative contribution of the four main sources to the total load in Redwell Creek, normalized to the total load in Redwell Creek. The category “all other sources” refers to the total of all other inputs, all of which are probably natural. Note that due to non-conservative behavior, the Zn loads at the prospect adit and Daisy Mine are minimum values, as is the SO_4^{2-} load at the Daisy Mine.

Table 1. Relative contribution of loads of Zn and SO_4^{2-} to Redwell Creek.

Source	Zn	SO_4^{2-}
Prospect adit	1.5%	2.0%
Artesian well	5.4%	10%
Red Well	2.9%	3.4%
Daisy Mine	66%	35%
All other sources	24%	49%

4 CONCLUSIONS

Through a program of spatially dense sampling and detailed chemical analyses, relative loads attributable to natural and anthropogenic sources can be estimated in alpine catchments. In the Redwell basin of central Colorado, approximately three-fourths of the total load of Zn and half the SO_4^{2-} are derived from anthropogenic sources. Similar estimates for Fe, Al, Mn, Cu, and Pb are more complicated because of the precipitation of Fe, Al, and Mn oxyhydroxide minerals and adsorption/coprecipitation of Cu and Pb.

Combining numerical modeling with detailed chemical measurements facilitates a more thorough understanding of the mechanisms of oxyhydroxide mineral formation and trace-metal sequestration. In stream reaches where model results predict precipitation of the oxyhydroxides, the same oxyhydroxides are observed to form. In general, Cu and Pb seem to be most strongly adsorbed or coprecipitated in the reaches where Al and Mn oxyhydroxides form, and they behave more conservatively in reaches where Fe oxyhydroxides form. This result is most likely due to pH effects rather than a preference for these metals for one type of solid over the other - the pH in the Al, Mn depositing reach is ~6, whereas it is <4 in the Fe-depositing reaches. In contrast to Cu and Pb, Zn shows nearly conservative behavior in most reaches.

REFERENCES

Briggs, P.H. 2002. The determination of twenty-seven elements in aqueous samples by inductively coupled plasma- atomic emission spectrometry. In J.E.Taggart, Jr. (ed.), *Analytical methods for chemical analysis of geologic and other materials*, U.S. Geological Survey: F1-F11. U.S. Geological Survey Open-file Report 02-223.

Ehlers, E.G. 1972. *The Interpretation of Geological Phase Diagrams*. San Francisco: W.H. Freeman & Co.

Fall, P.L. 1997. Timberline fluctuations and late Quaternary paleoclimates in the southern Rocky Mountains, Colorado. *Geol. Soc. Am. Bull.* 109(10): 1306-1320.

Furniss, G. & Hinman, N.W. 1998. Ferricrete provides record of natural acid drainage, New World district, Montana. In G.B. Arehart & J.R. Hulston (eds.), *Water-Rock Interaction 9*: 973-976. Rotterdam: Balkema.

Kimball, B.A., Runkel, R.L., Walton-Day, K. & Bencala, K.E. 2002. Assessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling: Cement Creek, Colorado, USA. *Appl. Geochem.* 17: 1183-1207.

Lamothe, P.J., Meier, A.L. & Wilson, S.A. 2002. The determination of forty-four elements in aqueous samples by inductively coupled plasma- mass spectrometry. In J.E.Taggart, Jr. (ed.), *Analytical methods for chemical analysis of geologic and other materials*, U.S. Geological Survey: H1-H11. U.S. Geological Survey Open-file Report 02-223.

May, H.M. 1992. The hydrolysis of aluminum: Conflicting models and the interpretation of aluminum geochemistry. In Y.K. Kharaka & A.S. Maest (eds.), *Proceedings of the 7th International symposium on Water-Rock Interaction*: 13-21. Rotterdam: Balkema.

Miller, W.R. & McHugh, J.B. 1999. Calculations of geochemical baselines of stream waters in the vicinity of Summitville, Colorado, before historic underground mining and prior to recent open-pit mining. In L.H. Filipek & G.S. Plumlee (eds.), *The Environmental Geochemistry of Mineral Deposits, Reviews in Economic Geology Volume 6B*: 505-514. Littleton, Colorado: Society of Economic Geologists.

Nordstrom, D.K. 1982. The effect of sulfate on aluminum concentrations in natural waters: some stability relations in the system $\text{Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ at 298 K: *Geochim. Cosmochim. Acta* 46: 681-692.

Parkhurst, D.L. & Appelo, C.A.J. 1999. User's guide to PHREEQC (version 2)- A computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99-4259.

Theodorakos, P.M., d'Angelo, W.M. & Ficklin, W.H. 2002. Fluoride, chloride, nitrate and sulfate in aqueous solution utilizing autosuppression chemically suppressed ion chromatography. In J.E.Taggart, Jr. (ed.), *Analytical methods for chemical analysis of geologic and other materials*, U.S. Geological Survey: V1-V7. U.S. Geological Survey Open-file Report 02-223.

Thomas, J.A. & Galey, J.T., Jr. 1982. Exploration and geology of the Mt. Emmons molybdenite deposits, Gunnison County, Colorado. *Econ. Geol.* 77: 1085-1104.

USGS 2004. National field manual for the collection of water-quality data. Website: <http://water.usgs.gov/owq/FieldManual/index.html>

Witte, K.M., Wanty, R.B. & Ridley W.I., in press. Engelmann Spruce (*Picea engelmannii*) as a biological monitor of changes in soil metal loading related to past mining activity. *Appl. Geochem.*

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